

The evolution of deep ocean chemistry and respired carbon in the Eastern Equatorial Pacific over the last deglaciation

Maria de la Fuente^{1,2}, Eva Calvo¹, Luke Skinner², Carles Pelejero^{1,3}, David Evans⁴,
Wolfgang Müller⁵, Patricia Povea⁶ and Isabel Cacho⁶

¹ *Institut de Ciències del Mar, CSIC, Barcelona, Spain;* ² *Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, UK;* ³ *Institució Catalana de Recerca i Estudis Avançats, Barcelona, Spain;* ⁴ *Department of Earth and Environmental Sciences, University of St Andrews, UK;* ⁵ *Department of Earth Sciences, Royal Holloway University of London, UK;* ⁶ *Grup de Recerca Consolidat en Geociències Marines, Departament de Dinàmica de la Terra i de l'Oceà, Universitat de Barcelona, Spain*

Corresponding author: Maria de la Fuente (md717@cam.ac.uk)

Key Points:

- Combined $[\text{CO}_3^{2-}]$, $\delta^{13}\text{C}$ and $\text{U}/\text{Ca}_\text{C}$ evidence indicates increased respired carbon storage in the last glacial maximum Eastern Equatorial Pacific
- Along with reduced deep-water ventilation, this evidence points to enhanced soft-tissue pump efficiency driven by ocean circulation changes
- Modest $[\text{CO}_3^{2-}]$ change suggests calcite dissolution as a further contribution to atmospheric CO_2 drawdown via increased ocean alkalinity

Abstract

It has been shown that the deep Eastern Equatorial Pacific (EEP) region was poorly ventilated during the Last Glacial Maximum (LGM) relative to Holocene values. This finding suggests a more efficient biological pump, which indirectly supports the idea of increased carbon storage in the deep ocean contributing to lower atmospheric CO₂ during the last glacial. However, proxies related to respired carbon are needed in order to directly test this proposition. Here we present *Cibicides wuellerstorfi* B/Ca ratios from ODP Site 1240 measured by laser-ablation inductively-coupled-plasma mass spectrometry (LA-IPCMS) as a proxy for deep water carbonate saturation state ($\Delta[\text{CO}_3^{2-}]$, and therefore $[\text{CO}_3^{2-}]$), along with $\delta^{13}\text{C}$ measurements. In addition, the U/Ca ratio in foraminiferal coatings has been analysed as an indicator of oxygenation changes. Our results show lower $[\text{CO}_3^{2-}]$, $\delta^{13}\text{C}$ and $[\text{O}_2]$ values during the LGM, which would be consistent with higher respired carbon levels in the deep EEP driven, at least in part, by reduced deep-water ventilation. However, the difference between LGM and Holocene $[\text{CO}_3^{2-}]$ observed at our site is relatively small, in accordance with other records from across the Pacific, suggesting that a ‘counteracting’ mechanism, such as seafloor carbonate dissolution, also played a role. If so, this mechanism would have increased average ocean alkalinity, allowing even more atmospheric CO₂ to be ‘sequestered’ by the ocean. Therefore, the deep Pacific Ocean very likely stored a significant amount of atmospheric CO₂ during the LGM, specifically due to a more efficient biological carbon pump, but also to an increase in average ocean alkalinity.

1. Introduction

Several marine carbon cycle mechanisms have been invoked to explain, at least, a major part of the atmospheric CO₂ drawdown observed over the last glacial period [e.g. *Kohfeld and Ridgwell*, 2009; *Sigman et al.*, 2010]. These mechanisms can be categorised broadly as deriving primarily from: 1) changes in whole ocean carbonate chemistry through global alkalinity (ALK) increase, for example due to ‘carbonate compensation’ or carbonate dissolution [e.g. *Archer and Maier-Reimer*, 1994]; 2) changes in the conditions or efficiency of air-sea gas exchange, i.e. changes in the ‘solubility pump’ [e.g. *Volk and Hoffert*, 1985]; or 3) changes in the accumulation of respired organic carbon (in the form of dissolved inorganic carbon, DIC) in the ocean interior, i.e. changes in the global average efficiency of the ‘soft-tissue’ component of the ‘biological carbon pump’ [e.g. *Volk and Hoffert*, 1985], either in absolute terms or relative to the global average efficiency of its ‘carbonate pump’ counterpart.

The efficiency of the soft tissue carbon pump was initially defined in terms of the gradient of major nutrient concentrations between the deep ocean and the shallow ocean, which arises due to the interplay of biological export from the surface ocean and the large-scale overturning circulation [*Volk and Hoffert*, 1985]. Due to the association of carbon with biologically fixed nutrients, the efficiency of the soft tissue pump relates directly to the DIC concentration gradient between the surface- and deep ocean (note that the two may become uncoupled due to air-sea

gas exchange effects, which affect carbon but not major nutrients). A more efficient glacial soft-tissue pump would therefore result in greater carbon storage in the deep sea and a lower surface ocean- and atmospheric $p\text{CO}_2$. This would occur as long as the soft tissue pump remained dominant over its carbonate pump counterpart (as it is in the modern ocean), as an efficient carbonate pump draws down surface ocean alkalinity and thus increases atmospheric CO_2 . Changes in the relative strength of the soft tissue and carbonate pumps would be driven by e.g. biological community structure driven DIC:ALK 'rain ratio' changes or water column remineralisation profile changes [Archer and Maier-Reimer, 1994; Kwon *et al.*, 2009]. Notably, a global average increase in soft-tissue pump efficiency can occur as a result of: 1) an increase in the biological flux of nutrients and carbon from the surface ocean to the deep interior, representing increased soft-tissue pump 'strength' [e.g. Martínez-García *et al.*, 2014]; and/or 2) a reduction in the return flux of remineralised nutrients and respired carbon from the deep interior to the surface ocean, for instance due to a weaker large-scale overturning circulation, representing reduced soft-tissue pump 'leakiness' [e.g. Toggweiler, 1999; Stephens and Keeling, 2000].

While a categorization of the various mechanisms for atmospheric CO_2 drawdown, as proposed above, might be useful for organising our thinking about past marine carbon cycle changes, it is important to emphasize that these mechanisms need not have operated in isolation from each other. For example, if an increase in soft-tissue pump global efficiency was achieved via a change in the ocean circulation, this would very likely co-occur with a change in the conditions of air-sea gas exchange and therefore the solubility pump. Furthermore, regardless of whether enhanced soft-tissue pump global efficiency is achieved via an increase in biological export rates or a reduction in the overturning circulation rate, it would lead to more respired carbon storage in the deep ocean, which in turn would lower deep ocean carbonate ion concentration ($[\text{CO}_3^{2-}]$), and $[\text{O}_2]$. If $[\text{CO}_3^{2-}]$ was reduced enough to cause seafloor carbonate dissolution (a mechanism also referred to as 'respiratory calcite dissolution' [Archer, 1991, 1996; Archer and Maier-Reimer, 1994]), it would eventually increase the whole ocean alkalinity budget and lead to further atmospheric CO_2 drawdown.

It has been proposed that increased export production in the EEP over the last glacial period played a role storing more respired carbon in the deep ocean than during the Holocene [e.g. Pichevin *et al.*, 2009; Robinson *et al.*, 2009; Doss and Marchitto, 2013]. However, other studies have argued against this [e.g. Winckler *et al.*, 2016; Costa *et al.*, 2016]. Glacial $[\text{O}_2]$ decrease in the deep EEP supports higher respired DIC accumulation [Bradtmiller *et al.*, 2010], although without elucidating the mechanism behind its variation. In this respect, it is now apparent that the EEP was less ventilated over the last part of the last glacial period, becoming better ventilated at the onset of the Heinrich Stadial 1 [de la Fuente *et al.*, 2015; Umling and Thunell, 2017]. This would indirectly support the idea of a more efficient biological pump during the last glacial due to a longer residence time for carbon in the deep ocean, thus reducing the leakiness of the biological pump and enhancing the deep ocean's respired carbon inventory.

In this study we set out to test the proposition that the respired carbon content of deep waters was indeed greater in the EEP during the LGM, as suggested by radiocarbon ventilation ages from this area [e.g. de la Fuente *et al.*, 2015]. Our

approach is to combine several respired carbon related proxies in the same sediment core ODP Site 1240 (hereafter referred to as ODP1240). Thus measurements of $\delta^{13}\text{C}$ and B/Ca have been performed on the calcite shells of the benthic foraminifer species *Cibicides wuellerstorfi* as a means of reconstructing respired nutrient and $[\text{CO}_3^{2-}]$ changes, respectively. B/Ca analyses have been proposed as a method for reconstructing past deep-water $[\text{CO}_3^{2-}]$ changes on the basis of an empirical correlation with deep water carbonate saturation state ($\Delta[\text{CO}_3^{2-}]$) [Yu and Elderfield, 2007], and on the assumption of invariant local saturation $[\text{CO}_3^{2-}]$ ($[\text{CO}_3^{2-}]_{\text{sat}}$). In addition, sedimentary redox conditions (i.e. estimates of changing $[\text{O}_2]$) have been reconstructed from analyses of U/Ca in the coatings (U/Ca_c; [Boiteau et al., 2012; Gottschalk et al., 2016]) of the planktonic species *Neogloboquadrina dutertrei*, and have been compared to existing authigenic uranium (aU; [Cochran et al., 1986; Bradtmiller et al., 2010; Jaccard et al., 2016]) measurements from the same area [Kienast et al., 2007; Bradtmiller et al., 2010]. Neither U/Ca_c nor aU have so far been shown to quantify changes in O_2 , and despite the fact that each of these approaches has its own limitations, we propose that their combination may offer robust qualitative information on glacial-interglacial bottom-water/pore-water $[\text{O}_2]$ changes.

2. Materials and methods

2.1. EEP hydrographic settings

Sediment core ODP1240 was recovered from the southern edge of the Panama Basin in the EEP (0°01.31' N, 86°27.76' W) at 2,921 m water depth (Figure 1). The chronostratigraphy for this sediment core was previously described by *de la Fuente et al.* [2015], and is based on sediment depth-age modeling using calibrated radiocarbon dates on *Neogloboquadrina dutertrei* that have been corrected for a variable reservoir age offsets, constrained through stratigraphic alignment of the $\text{U}_{\text{K}^{37}}$ record from ODP1240 with Greenland $\delta^{18}\text{O}$ records. The hydrography of the EEP, in common with the whole tropical Pacific, is highly influenced by Southern Ocean water masses at depth [Strub et al., 1998; Kessler, 2006], with the depth of ODP1240 location, in particular, currently bathed by a mixture of Upper Circumpolar Deep Water (UCDW) and Pacific Deep Water (PDW; Figure 1). PDW refers to the water mass formed at depth in the North Pacific through very slow vertical mixing of bottom and intermediate waters of southern origin and extremely long residence times, and UCDW represents the upper layer of the deep water mass flowing within the Antarctic Circumpolar Current (ACC), a mixture of deep and re-circulated waters from the Atlantic, Indian and Southern Oceans [Mantyla and Reid, 1983; You, 2000]. Although these deep water masses have different origins, both occupy approximately the same density and depth range in the Pacific [Talley et al., 2011] as a consequence of the extremely weak deep circulation in the Pacific Ocean. An additional feature of the modern Panama Basin hydrography is a degree of 'biogeochemical aging' in its deepest part. Although this points to the possibility of highly localized influences on respired carbon in the Panama Basin, such influences do not affect the basin as a whole and are relatively small, with hardly any influence the at location of ODP1240 today.

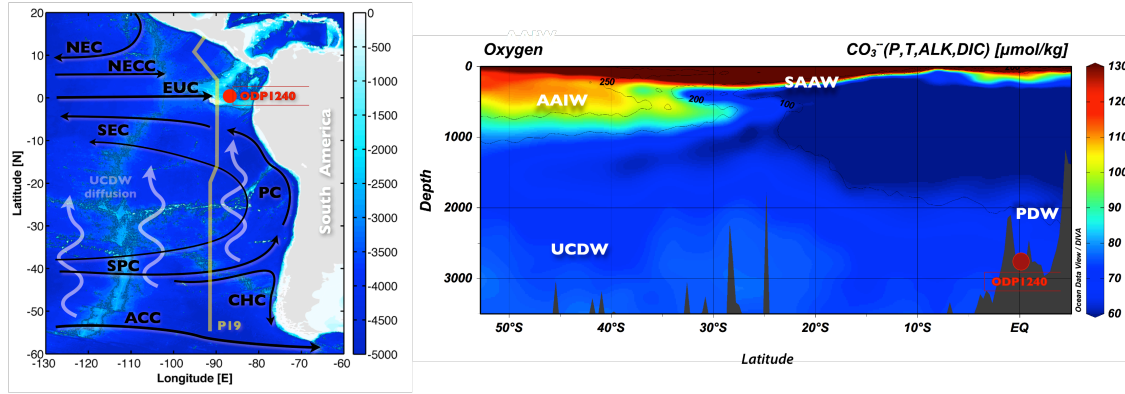


Figure 1. EEP hydrography. In the left panel, map of the study area displaying the bathymetry (blue scale), the location of the sediment core ODP1240 (red dot), the WOCE P19 transect (light yellow meridional line), and a scheme of the upper (black arrows) and deep (purple arrows) ocean circulation of the area: North Equatorial Current (NEC), North Equatorial Countercurrent (NECC), Equatorial Undercurrent (EUC), South Equatorial Current (SEC), Peru Current (PC), South Pacific Current (SPC), Cape Horn Current (CHC), Antarctic Circumpolar Current (ACC) and the northward diffusion of the Upper Circumpolar Deep Water mass (UCDW). In the right panel, vertical section of the WOCE P19 transect showing modern $[\text{CO}_3^{2-}]$ (colour scale) and oxygen (contours) [Schlitzer, 2017]. Water masses are indicated: Antarctic Intermediate Water (AAIW), UCDW, Subantarctic Water (SAAW) and Pacific Deep Water (PDW).

2.2. B/Ca analysis by LA-ICPMS and $[\text{CO}_3^{2-}]$ estimates

The epibenthic foraminifer *C. wuellerstorfi* was picked from 15 samples from the top three meters of sediment core ODP1240 covering the last ~30 kyr. Each sample was composed of ~6 specimens (>212 μm) that were rinsed in milliQ water and secured on a double-sided carbon tape on a glass slide for LA-ICPMS analysis. Between 2-3 depth-profiling ablations were made per shell using the RESolution M-50 prototype 193nm ArF laser ablation system (featuring a two-volume Laurin LA cell) coupled to an Agilent 7500ce quadrupole ICPMS at Royal Holloway University of London [Müller *et al.*, 2009]. Ablation was performed using a laser spot size of 96 μm , repetition rate of 2 Hz and fluence of ~4 J/cm². Data quantification follows [Longerich *et al.*, 1996] with the transformation of raw count rates to concentration achieved using ⁴³Ca as an internal standard and NIST610/612 as a calibration standard. The accuracy and precision of B/Ca measurements using these conditions is <5 and <10% respectively (see Evans *et al.* [2015]). Several steps to exclude any possible contaminant phases from the data were applied [Boyle, 1983; Bolton *et al.*, 2011; Marr *et al.*, 2011], and spots with B/Ca values higher than the individual foraminifer average plus 2SD were removed and not included in further palaeoclimatic interpretations. A more detailed discussion of the methodology can be found in the Supporting Information [Eggins *et al.*, 1998; Jochum *et al.*, 2006; Jochum *et al.*, 2011; Evans and Müller, 2013; Müller and Fietzke, 2016].

C. wuellerstorfi B/Ca ratios have been experimentally shown to linearly relate to $\Delta[\text{CO}_3^{2-}]$ based on global core-top measurements in the modern ocean, as described by equation 1 below [Yu and Elderfield, 2007], thereby allowing downcore $[\text{CO}_3^{2-}]$ to be estimated from equation 2, albeit with some caution.

$$\Delta[\text{CO}_3^{2-}] = (\text{B/Ca} - 177.1)/1.14 \text{ (in } \mu\text{mol/mol)} \quad (1)$$

$$\Delta[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_{\text{sat}} \quad (2)$$

Seawater $[\text{CO}_3^{2-}]_{\text{sat}}$ in the modern ocean is estimated from water column $[\text{CO}_3^{2-}]/\Omega_{\text{calcite}}$ data, where Ω_{calcite} is the calcite saturation state in seawater ($\Omega_{\text{calcite}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]/K_{\text{sp}}$, and K_{sp} is the solubility product of calcite ($[\text{Ca}^{2+}]_{\text{sat}} \cdot [\text{CO}_3^{2-}]_{\text{sat}}$) at a given temperature, salinity and pressure). However, seawater $[\text{CO}_3^{2-}]_{\text{sat}}$ in the deep ocean is typically assumed to have remained constant over the late Pleistocene since the influence of pressure, bottom water temperature and salinity in the past are thought to have exerted little effect on $[\text{CO}_3^{2-}]_{\text{sat}}$ over this time period [Allen *et al.*, 2015]. Thus, the general equation to estimate downcore $[\text{CO}_3^{2-}]$ through B/Ca ratios measured in the calcite shell of *C. wuellerstorfi* would be:

$$[\text{CO}_3^{2-}] = ((\text{B/Ca} - 177.1)/1.14) + ([\text{CO}_3^{2-}]_{\text{(mod)}}/\Omega_{\text{calcite (mod)}}) \quad (3)$$

In this study, modern $[\text{CO}_3^{2-}]$ and Ω_{calcite} have been inferred from instrumental measurements of ALK and DIC available from the GLODAP dataset (WOCE P19C transect; Tsuchiya and Talley, [1998]). For these estimates, the CO2SYS software package [Lewis *et al.*, 1998; Pierrot *et al.*, 2006] and the equilibrium constants from Mehrbach *et al.* [1973] and Dickson and Millero [1987] were used. The obtained modern values at a depth of 2,888 m were 67.7 $\mu\text{mol/kg}$ for $[\text{CO}_3^{2-}]$ and 0.9 for Ω_{calcite} , leading to a modern $[\text{CO}_3^{2-}]_{\text{sat}}$ of 75.2 $\mu\text{mol/kg}$ (station: 18373; LAT: 0.004° N; LONG: 85.84° W).

Since the initial calibration of Yu and Elderfield [2007] was published, several studies have provided additional core-top measurements, but only one provided B/Ca results analysed by LA-ICPMS [Raitzsch *et al.*, 2011]. In order to add further support to this technique, B/Ca ratios in *C. wuellerstorfi* specimens have been analysed here in nine core-top samples across the Atlantic Ocean by LA-ICPMS, following the same scheme described above for downcore analyses. Estimates of modern $\Delta[\text{CO}_3^{2-}]$ were obtained using either in situ data from the corresponding cruises when available, or data from nearby GLODAP sites [Key *et al.*, 2004], in both cases by deriving values for modern $[\text{CO}_3^{2-}]$ and Ω_{calcite} (Table S1 in the Supporting Information).

2.3. $\delta^{13}\text{C}$ measurements

Down-core $\delta^{13}\text{C}$ measurements were performed on 46 samples from ODP1240, covering the last 25 kyr and consisting exclusively of *C. wuellerstorfi* individuals from the >212 μm fraction size. The analyses were performed using a Thermo Kiel device attached to a Thermo MAT253 Mass Spectrometer in dual inlet mode at the University of Cambridge. The sample size was $\sim 100 \mu\text{g}$, with the exception of a few samples of 20 μg , which is close to the detection limit of this machine. A few additional $\delta^{13}\text{C}$ measurements in *C. wuellerstorfi* from ODP1240, consisting of four to five specimens each (also from the >212 μm size fraction) were obtained at the Scientific and Technological Center of the University of Barcelona (CCiT-UB) by using a FinniganMAT252 mass spectrometer fitted with a Kiel Carbonate Device I. All $\delta^{13}\text{C}$ values presented here are reported as per mil relative to the international

standard Vienna Pee Dee Belemnite (VPDB), with a typical external reproducibility estimated to be equal or better than $\pm 0.06\text{‰}$ and $\pm 0.03\text{‰}$ for the Universities of Cambridge and Barcelona, respectively.

2.4. U/Ca analysis in planktonic foraminiferal coatings

U/Ca ratios measured in the foraminiferal shell coatings have been suggested to reflect changes in the sedimentary redox conditions and therefore potentially linked with changes in the $[\text{O}_2]$ in bottom waters [Boiteau *et al.*, 2012]. This oxygen related proxy is based on the redox chemistry of U in seawater, shifting from the soluble form U(VI) in oxygenated waters to the insoluble U(IV) species as the medium depletes in oxygen [Langmuir, 1978; Cochran *et al.*, 1986; Morford and Emerson, 1999].

In order to quantify the U concentration in the foraminiferal coatings, clays were removed and an acid leach step to remove any adsorbed ions was performed in 20 *N. dutertrei* samples, each one composed of ~ 30 specimens collected from the 212-300 μm fraction. No oxidative or reductive step was performed in order to preserve the thin coating layer [Boiteau *et al.*, 2012]. Cleaned samples were dissolved in 0.1M HNO_3 , diluted to 10 ppm Ca^{2+} and analysed by ICP-MS at the University of Cambridge using a Thermo Element XR, with a typical analytical reproducibility of $\sim 7\%$.

3. Results

3.1. *C. wuellerstorfi* B/Ca core-top measurements by LA-ICPMS

In Figure 2, *C. wuellerstorfi* B/Ca analyses from the Atlantic Ocean core-tops are compared to their corresponding $\Delta[\text{CO}_3^{2-}]$ values, as well as to other core-top data available from the literature [Yu and Elderfield, 2007; Brown *et al.*, 2011; Rae *et al.*, 2011; Raitzsch *et al.*, 2011; Yu *et al.*, 2013].

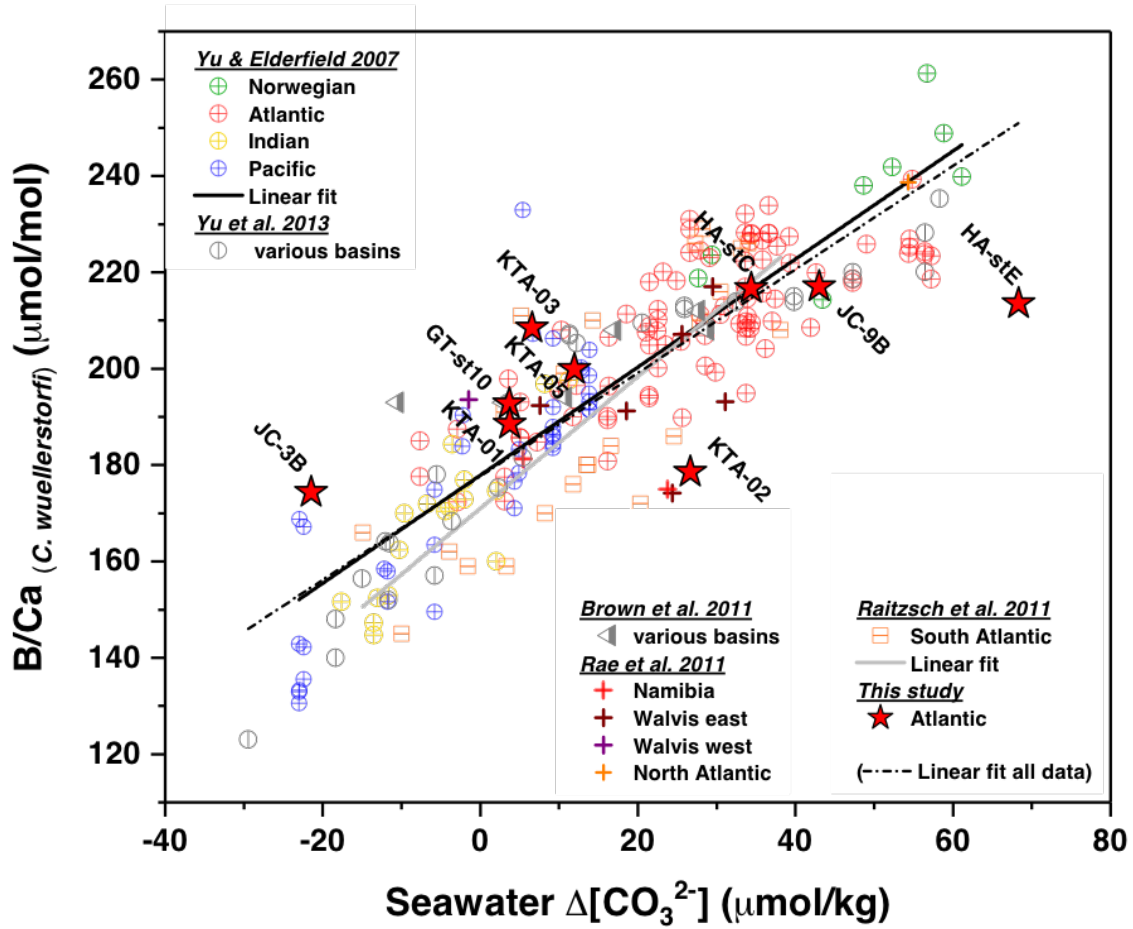


Figure 2. Bottom water $\Delta[\text{CO}_3^{2-}]$ vs B/Ca ratios in *C. wuellerstorfi* from core-top samples analysed by solution-ICPMS [Yu and Elderfield, 2007; Brown et al., 2011; Rae et al., 2011; Yu et al., 2013] and by LA-ICPMS [Raitzsch et al. 2011] and core-tops from the Atlantic Ocean analysed in this study (red stars)]. Black solid line represents the linear fit from Yu and Elderfield [2007] by solution-ICPMS, while grey solid line represents the linear fit from Raitzsch et al. [2011] by LA-ICPMS. Black dashed line represent the linear fit from all the records together including the core-tops analysed in this study.

The core-top measurements presented here fit well within the two existing linear regressions from Yu and Elderfield [2007] ($A=1.14$; $B=177.1$) and from Raitzsch et al. [2011] ($A=1.37$; $B=170.9$), and combining all of the data results in an indistinguishable new calibration equation (~ 230 core top samples including this study; $A=1.07$; $B=177.7$), thus providing support for B/Ca as a proxy for $\Delta[\text{CO}_3^{2-}]$ and for LA-ICPMS as a suitable technique for this type of analysis. The original calibration equation from Yu and Elderfield [2007] is adopted here for downcore $\Delta[\text{CO}_3^{2-}]$ estimates in ODP1240 for better comparison with previously published data.

3.2. B/Ca- $[\text{CO}_3^{2-}]$, $\delta^{13}\text{C}$ and U/Ca_c downcore ODP1240

Downcore B/Ca ratios from *C. wuellerstorfi* in ODP1240 core are $\sim 10 \mu\text{mol/mol}$ lower over the end of the last glacial period (~ 18 -23 kyr), with an average of $\sim 172 \pm 5 \mu\text{mol/mol}$ ($\pm 1\text{SE}$), than across the mid-late Holocene (~ 0 -8 kyr), which

exhibits values of $\sim 182 \pm 4$ $\mu\text{mol/mol}$ ($\pm 1\text{SE}$) (Figure 3a). When converted into $[\text{CO}_3^{2-}]$ the difference between glacial (~ 71 $\mu\text{mol/kg}$) and interglacial (~ 80 $\mu\text{mol/kg}$) is ~ 9 $\mu\text{mol/kg}$, which is not as large as might be expected based on observed radiocarbon ventilation changes, possibly as a result of other processes that we discuss in the next sections. *C. wuellerstorfi* $\delta^{13}\text{C}$ measurements from ODP1240 are also characterised by lower values during the LGM compared to the Holocene of ~ 0.4 ‰, showing good consistency between measurements performed in the two laboratories (Figure 3b). Although both $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$ seem to be in good agreement and exhibit a similar pattern across the deglaciation, a ‘bump’ just before the termination onset is observed only in the $[\text{CO}_3^{2-}]$ record. This may reflect processes that have an impact exclusively in $[\text{CO}_3^{2-}]$ without modifying $\delta^{13}\text{C}$ (i.e. changes in seafloor carbonate dissolution), or analysis artefacts in those specific samples. Although we cannot discard any of these possibilities unequivocally, the observed change in $[\text{CO}_3^{2-}]$ before the deglaciation seems to be too rapid to be explained by variations in calcite dissolution. U/Ca_C measurements in the planktonic species *N. dutertrei* show higher values at the LGM compared to the Holocene suggesting, very likely, a more reducing environment at the water-sediment boundary at that time, and therefore lower $[\text{O}_2]$, in the deep EEP (Figure 3c).

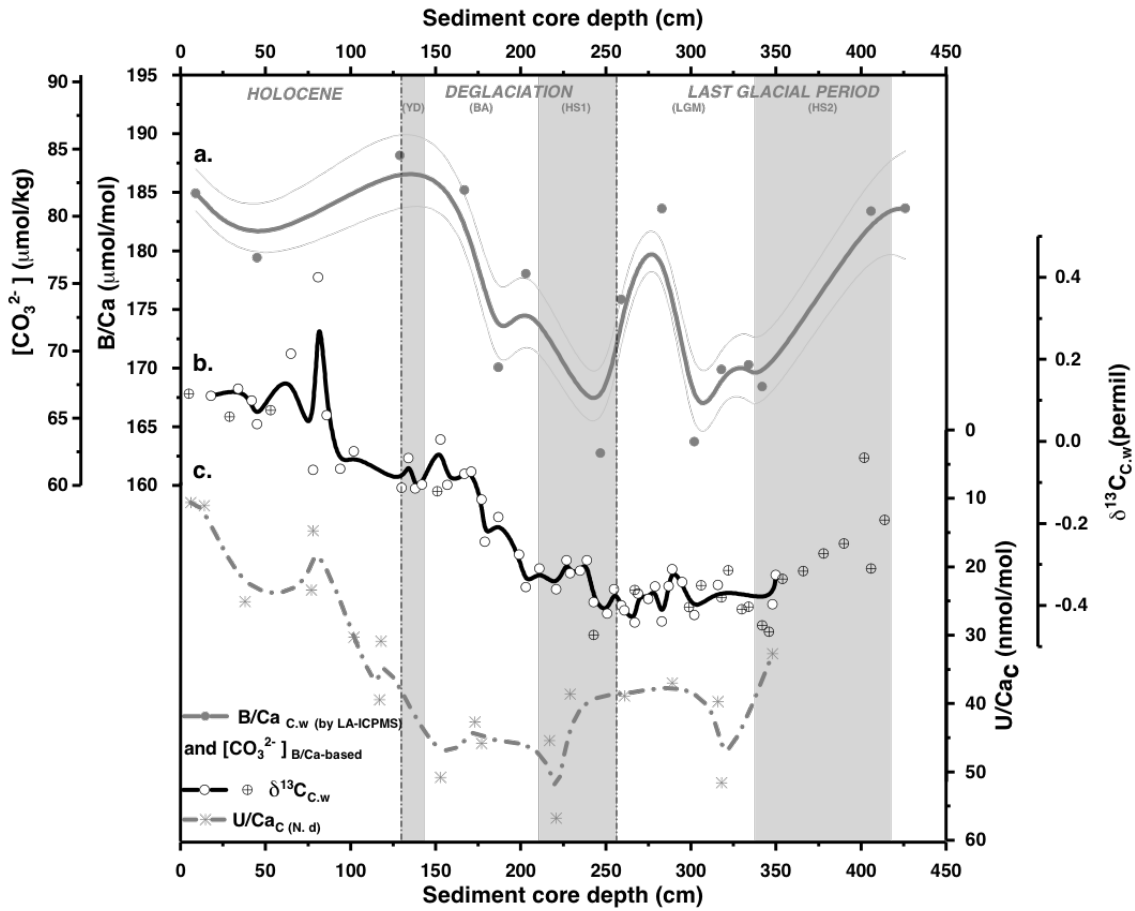


Figure 3. Deep water respired carbon related records across the first 450 cm of the sediment core ODP1240 (last ~ 30 kyr). a) B/Ca ratios in *C. wuellerstorfi* measured by LA-ICPMS and $[\text{CO}_3^{2-}]$ derived estimates (grey solid line/dots). Uncertainties represent ± 1 SE in $[\text{CO}_3^{2-}]$ (grey envelope). $[\text{CO}_3^{2-}]$ was

estimated by using the calibration equation from *Yu and Elderfield* [2007] and assuming a constant $[\text{CO}_3^{2-}]_{\text{sat}}$ value of $75.2 \mu\text{mol/kg}$ (estimated from modern $[\text{CO}_3^{2-}]$ and Ω_{Calcite} values from the GLODAP dataset WOCE P19 transect, see main text). b) Benthic $\delta^{13}\text{C}$ from *C. wuellerstorfi* (black line/solid dots and crossed dots analysed at the Universities of Cambridge and Barcelona, respectively). c) U/Ca ratios in the coatings of *N. dutertrei* (grey dashed line/asterisks). All lines are B-spline smoothed. Vertical dashed lines delimit relevant climatic periods, and light grey vertical bands highlight the coldest periods of the last 30 kyr. HS1 and HS2: Heinrich Stadial 1 and 2 respectively; BA: Bølling-Allerød; YD: Younger Dryas.

4. Discussion

4.1. A comparison of ocean ventilation and carbonate system changes in the EEP across the last deglaciation

A poorly ventilated deep EEP at the end of the last glacial period compared to the present has been shown by the radiocarbon offsets between benthic foraminifera and atmospheric records (B-Atm) [*de la Fuente et al.*, 2015]. This study also revealed that better ventilation of this area of the Pacific began at the onset of the deglaciation (~ 17.5 kyr BP), demonstrating a consistency with other ventilation records from the South Pacific [*Sikes et al.*, 2000; *Siani et al.*, 2013; *Skinner et al.*, 2015] and the Atlantic sector of the Southern Ocean [*Skinner et al.*, 2010; *Burke and Robinson*, 2012], all of which broadly co-varied in time with changes in atmospheric $\Delta^{14}\text{C}$ and CO_2 . Thus, when CO_2 increased and $\Delta^{14}\text{C}$ decreased in the atmosphere at the deglaciation onset (Figure 4a,b, respectively), all of these deep water ventilation records start to exhibit enhanced ventilation (Figure 4c, *de la Fuente et al.* [2015] and figures therein). This observation has at least two important implications: 1) that the deglacial increase in atmospheric CO_2 might be directly and causally linked to the deglacial evolution of deep ocean ventilation; and 2) that the deep ocean, including the EEP, might have contained a higher concentration of respired CO_2 during the glaciation as compared to the late Holocene and thus acted as a source of carbon to the atmosphere during deglaciation.

In the absence of major ocean interior carbon sources, radiocarbon behaves as a semi-conservative tracer that is not significantly affected by biological or chemical reactions within the ocean, and tracks the mean time since a water mass exchanged carbon with the atmosphere. Radiocarbon ventilation estimates therefore allow us to isolate the contribution of ocean ventilation to changes in the global average efficiency of the soft-tissue pump. Increased radiocarbon ventilation ages observed in ODP1240 during the last late glacial period could therefore imply an increase in the amount of remineralised/oxidised organic matter in the ocean interior, i.e. more carbon respired by microorganisms per unit volume due to more time for this respired carbon to accumulate. If this happened, the most noticeable consequences might be, on the one hand, a decrease in seawater $\delta^{13}\text{C}$ due to enhanced lighter carbon isotope (^{12}C) release, and on the other hand, a greater CO_2 accumulation in seawater as a product of respiration. Such an increase in seawater $[\text{CO}_2]$ would have altered the carbonate system equilibrium, leading to a drop in $[\text{CO}_3^{2-}]$ in order to buffer the change in seawater pH [*Zeebe and Wolf-Gladrow*, 2001; *Sarmiento and Gruber*, 2004; *Williams and Follows*, 2011].

The $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$ results presented here from ODP1240 are in good agreement with these expectations (Figure 4d,e), as well as with a previous study in the area [Doss and Marchitto, 2013], showing lower $\delta^{13}\text{C}$ and $[\text{CO}_3^{2-}]$ during the late glacial, in parallel with reduced radiocarbon ventilation, and an increase in all of these parameters across the deglaciation. Interestingly, when the modern $[\text{CO}_3^{2-}]$ value from this area is taken into account, a drop at the late Holocene is inferred. The existence of such $[\text{CO}_3^{2-}]$ decrease across the late Holocene has been previously suggested on the basis of sediment composition data and modeling studies [Broecker and Peng, 1987; Berelson *et al.*, 1997]. This feature might reflect a restored lower average ocean alkalinity due to enhanced carbonate preservation associated with the release of excess respired carbon from the ocean interior to the atmosphere during deglaciation, which in turn might have helped to maintain the higher CO_2 in the atmosphere during the late Holocene. However, another plausible explanation for the late Holocene-modern value ‘mismatch’ observed in our core might be related to the inherent noise contained in the B/Ca- $\Delta[\text{CO}_3^{2-}]$ calibration applied. Indeed, this issue has been observed in previous studies that estimated $[\text{CO}_3^{2-}]$ through B/Ca analysis in benthic foraminifera [Yu *et al.*, 2008, 2013; Allen *et al.*, 2015; Elmore *et al.*, 2015]. In order to avoid this mismatch, some of these studies opted for applying a correction by subtracting the core top value to each measurement downcore, thus forcing the record to fall on the regression line given by the equation: $[\text{CO}_3^{2-}]_{\text{downcore}} = [\text{CO}_3^{2-}]_{\text{pre-industrial}} + \Delta(\text{B/Ca})/1.14$, where $\Delta(\text{B/Ca})$ represents the deviation of each downcore sample relative to the core-top value [Yu *et al.*, 2008, 2010, 2013, 2014b, 2016]. However, in our study, the conventional option of applying the linear correlation from Yu and Elderfield [2007] without correcting for the core-top value has been chosen to avoid applying arbitrary offsets to the dataset. This issue would call for cautious approach when considering absolute $[\text{CO}_3^{2-}]$ values derived from benthic B/Ca analysis, and may suggest that relative changes observed down-core might be more robust than inter-core or absolute value comparisons. It would also call for a careful interpretation when using data for any further carbonate system calculations.

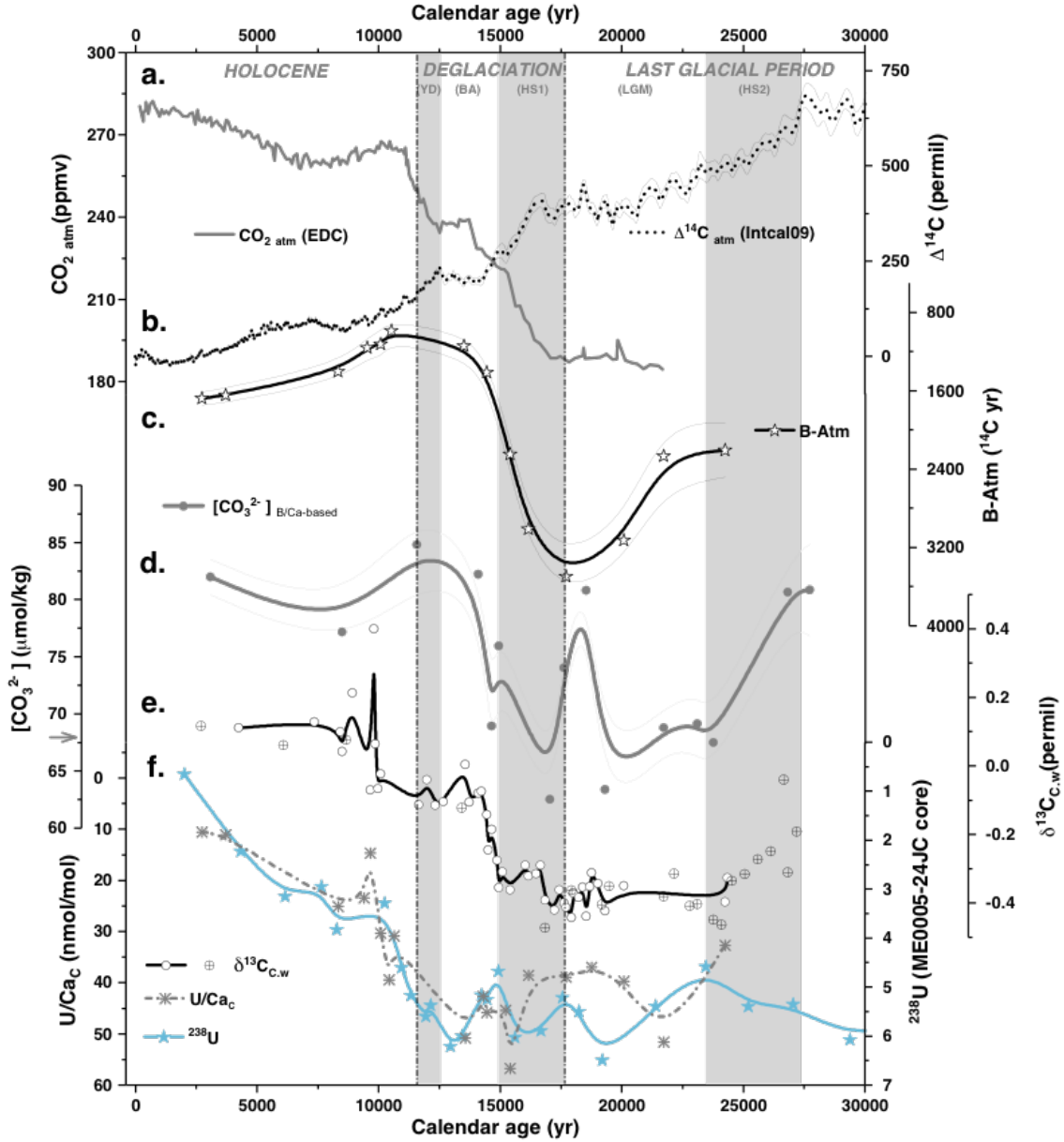


Figure 4. Comparison of deep ocean records from ODP1240 with records of atmospheric CO_2 and radiocarbon activity over the last 30 kyr. a) Atmospheric CO_2 concentrations from EPICA Dome C (EDC) ice core (for the deglacial period, Monnin *et al.*, [2001]; for the Holocene period, Flückiger *et al.*, [2002]), placed on the age scale of Lemieux-Dudon *et al.* [2010] (grey line). b) Atmospheric radiocarbon activity ($\Delta^{14}\text{C}$) changes (IntCal09 calibration curve; Reimer *et al.*, [2009] (black dotted line). c) Deep-water ventilation reconstruction (B-Atm, from SST alignment in de la Fuente *et al.* [2015]) (black line/white stars). d) $[\text{CO}_3^{2-}]_{\text{B/Ca-based}}$ (\pm SE) (grey solid line/dots). e) $\delta^{13}\text{C}$ from *C. wuellerstorfi* (black line/solid dots and crossed dots analysed at the Universities of Cambridge and Barcelona, respectively). f) Oxygenation proxies: $\text{U}/\text{Ca}_\text{C}$ from *N. dutertrei* (grey dashed line/asterisks) and ^{238}U from ME0005-24JC (same location as Site 1240; blue line/stars; Kienast *et al.*, [2007]; Bradtmiller *et al.*, [2010]). All lines are B-spline smoothed. Vertical dashed lines delimit relevant climatic periods, and light grey vertical bands highlight the coldest periods of the last 30 kyr. The grey arrow on the $[\text{CO}_3^{2-}]$ axis represents the modern water value ($67.6 \mu\text{mol/kg}$) obtained from GLODAP database (WOCE P19C transect; Tsuchiya and Talley, [1998]).

Another consequence of the hypothetical increase in respired carbon due to a longer residence time of deep water during the LGM would be a drop in $[\text{O}_2]$, as microorganisms consume O_2 during respiration of organic matter. Following

reformulations of the traditional Redfield ratios of remineralised organic matter [Redfield *et al.*, 1963], the release of 117 CO₂ molecules consumes 170 molecules of O₂ [Anderson and Sarmiento, 1994]. Our U/C_{ac} results show the expected depletion in O₂ if the respired carbon content of the ocean interior was indeed higher at the LGM compared to the Holocene (Figure 4f). Moreover, our qualitative relative oxygenation changes indicated by U/C_{ac} estimates support previous measurements of authigenic uranium (aU) in core ME0005-24JC (recovered from nominally the same location as Site 1240; Kienast *et al.*, [2007]) showing a similar trend, characterised by higher aU (i.e. lower O₂) during the glacial compared to the Holocene [Kienast *et al.*, 2007; Bradtmiller *et al.*, 2010] (Figure 4f).

Thus, all records presented here, i.e. [CO₃²⁻], δ¹³C and oxygenation proxies, are in good agreement with the deep radiocarbon ventilation in the EEP, and lend support to the hypothesis of a higher efficiency of the biological pump during the LGM due to changes in its leakiness. In the same way, all of these records are in reasonably close agreement through deglaciation, increasing as the deep EEP gets better ventilated at the onset of the last termination. Despite this general agreement, it is interesting to note that both oxygenation proxies, aU and U/C_{ac}, do not change synchronously with the rest of the proxies at the beginning of the deglaciation, but later at the termination. A plausible explanation for this apparent mismatch might rely on a decoupling of pore-water and deep water chemistry, for example due to a productivity pulse between ~17-14 kyr [e.g. Calvo *et al.*, 2011] that would have depleted O₂ in the pore-fluids of the sediment (which the oxygenation proxies would record), even after the radiocarbon ventilation and carbonate saturation of the ambient deep-water started to increase. Taken together, all the records presented here point to the deep EEP as a plausible contributor to the decreased atmospheric CO₂ during the LGM, by storing more respired carbon at the expense of the surface ocean and atmospheric carbon inventories, that was posteriorly released during the deglaciation once the ocean interior got better ventilated.

A different interpretation based on similar glacial-interglacial Δ[CO₃²⁻] changes, also from the Panama Basin, has been proposed by Doss and Marchitto, [2013]. This study suggests that the observed glacial Δ[CO₃²⁻] difference found between a sediment core located at the sill depth and sediment cores located deeper in the basin are indicative of an increase in the export production during the last glacial. While we do not discard this possibility, which must eventually be tested against other evidence for increased export production during the last glacial period, we propose that it must have acted in addition to a decrease in ocean ventilation, as indicated by our combined proxy results, including radiocarbon ventilation ages. Below we discuss the available evidence for other possible contributions to the apparent increase in the respired carbon content of the deep EEP, including more direct nutrient-based indicators of export production.

4.2. Export production as a complementary mechanism for a higher biological pump efficiency in the EEP

An increase in the strength of the biological pump (i.e. export production rates) could have operated on the glacial atmospheric CO₂ drawdown independently of,

or in addition to, contributions from changes in ocean ventilation constrained using radiocarbon measurements. The glacial changes observed in deep ocean [CO_3^{2-}], $\delta^{13}\text{C}$ and oxygenation records from ODP1240, described in the previous subsection, might indeed be compatible with an increase in surface productivity over the LGM. Thus, a larger flux of organic matter to the deep ocean in this area might have contributed to the observed drop in [CO_3^{2-}] and $\delta^{13}\text{C}$, as a consequence of higher levels of carbon respiration that would have also increased the release of respired CO_2 to deep water and the consumption of dissolved O_2 .

The documented increase in dust-borne iron delivery to the iron-limited low-latitude Pacific Ocean at the last glacial period [McGee *et al.*, 2007] has led to a number of investigations into a potential increase in surface productivity over this period, however, with ambiguous results. On the one hand, lower opal $\delta^{30}\text{Si}$ content in ODP1240 as a proxy for the relative utilization of silica during the glacial has been interpreted as an indication of a decline in the Si:C uptake ratio by diatoms due to an iron-replete glacial ocean, which would be compatible with the assumption of higher productivity over this period [Pichevin *et al.*, 2009]. Similarly, nitrogen isotopes ($\delta^{15}\text{N}$) from bulk sediments in ODP1240 core, once they are corrected for denitrification effects typical of the Central American margin, showed higher values over the LGM compared to the Holocene suggesting higher local nutrient consumption consistent with higher surface productivity over the LGM [Robinson *et al.*, 2009]. At the same time, higher abundances of organic biomarkers (alkenones and brassicasterol) have been shown in the same core during the LGM, as compared to the present [Calvo *et al.*, 2011]. However, these inferences are contradicted by other studies that do not support the proposed increase in the strength of the biological pump in the EEP as a mechanism for the atmospheric CO_2 drawdown during the LGM [Bradt Miller *et al.*, 2006; Kienast *et al.*, 2006]. More recently, for instance, Winckler *et al.* [2016] reported excess Ba and opal fluxes obtained from sediment cores located along the equatorial Pacific, which do indicate higher productivity in this area (stimulated by an increased Fe supply by upwelling rather than by dust deposition), but with peak export occurring during deglaciation rather than over the LGM. Moreover, Costa *et al.* [2016] suggested that the glacial dust supply to the equatorial Pacific exerted a negligible effect on surface productivity, arguing that the major nutrient supply with Southern Ocean origin was actually reduced as nutrients were mostly consumed in the Subantarctic Zone.

An increase in organic carbon (C_{org}) accumulation rates in the EEP over the LGM has been documented in core ODP1240 [Pichevin *et al.*, 2009], as well as in the nearby core P6 [Pedersen, 1983]. Such higher C_{org} accumulation might have been the result of an increase in surface productivity, but also the result of better preservation of the organic matter due to lower oxygen content in the deep ocean at that time. Thus, in light of the fact that existing proxy reconstructions can neither corroborate nor rule out unequivocally an increase in EEP surface productivity over the LGM, two key questions remain: was the observed increase in the biological pump efficiency in the glacial EEP mainly due to changes in ocean circulation, or changes in the carbon export production in this area; how much did the proposed increase in organic carbon export production affect carbon storage in the deep ocean? Arguably these questions cannot be fully resolved without accurate quantitative estimates of export production and deep ocean apparent

oxygen utilization changes. Nevertheless, it is clear at least that ocean ventilation changes made some contribution, though only qualitative conclusions, such as those drawn above, are possible at present.

4.3. Carbonate seafloor dissolution as a potential counteracting mechanism for $[\text{CO}_3^{2-}]$ EEP changes

A decrease in deep ocean ventilation along with a potential increase in carbon export production in the EEP at the LGM are therefore proposed as the mechanisms responsible for the decrease in deep $[\text{CO}_3^{2-}]$, $\delta^{13}\text{C}$ and oxygenation observed in this area. The action of any of these mechanisms (alone or together) might be expected, in principle, to achieve a relatively large $[\text{CO}_3^{2-}]$ glacial-Holocene difference. For example, spatial correlations of radiocarbon and $[\text{CO}_3^{2-}]$ in the modern deep ocean would predict a change of $\sim -37 \mu\text{mol/kg}$ for the ~ 960 ^{14}C -yr increase in deep water radiocarbon ventilation observed in ODP1240 at the LGM relative to the modern ocean [Key *et al.*, 2004]. However, the results from this study indicate only a small $[\text{CO}_3^{2-}]$ change between these two periods ($\sim 9 \mu\text{mol/kg}$), suggesting that a counteracting mechanism, such as seafloor respiratory calcite dissolution, might have also played a role: when carbonate dissolves in seawater, both $[\text{CO}_3^{2-}]$ and ALK increase [Broecker and Peng, 1989; Zeebe and Wolf-Gladrow, 2001]. If this was the case, a decrease in the CaCO_3 content in sediments might be initially expected. However, $\text{CaCO}_3\%$ from ODP1240 indicates little change between 25-15 kyr (Figure 5). Furthermore, the possibility of an increase in the calcium carbonate export production rates as a masking mechanism for the expected $\text{CaCO}_3\%$ drop seems not to be supported by carbonate flux data (expressed as $^{230}\text{Th}\text{-CaCO}_3$) from this area, which also show little change between last glacial and Holocene (Figure 5).

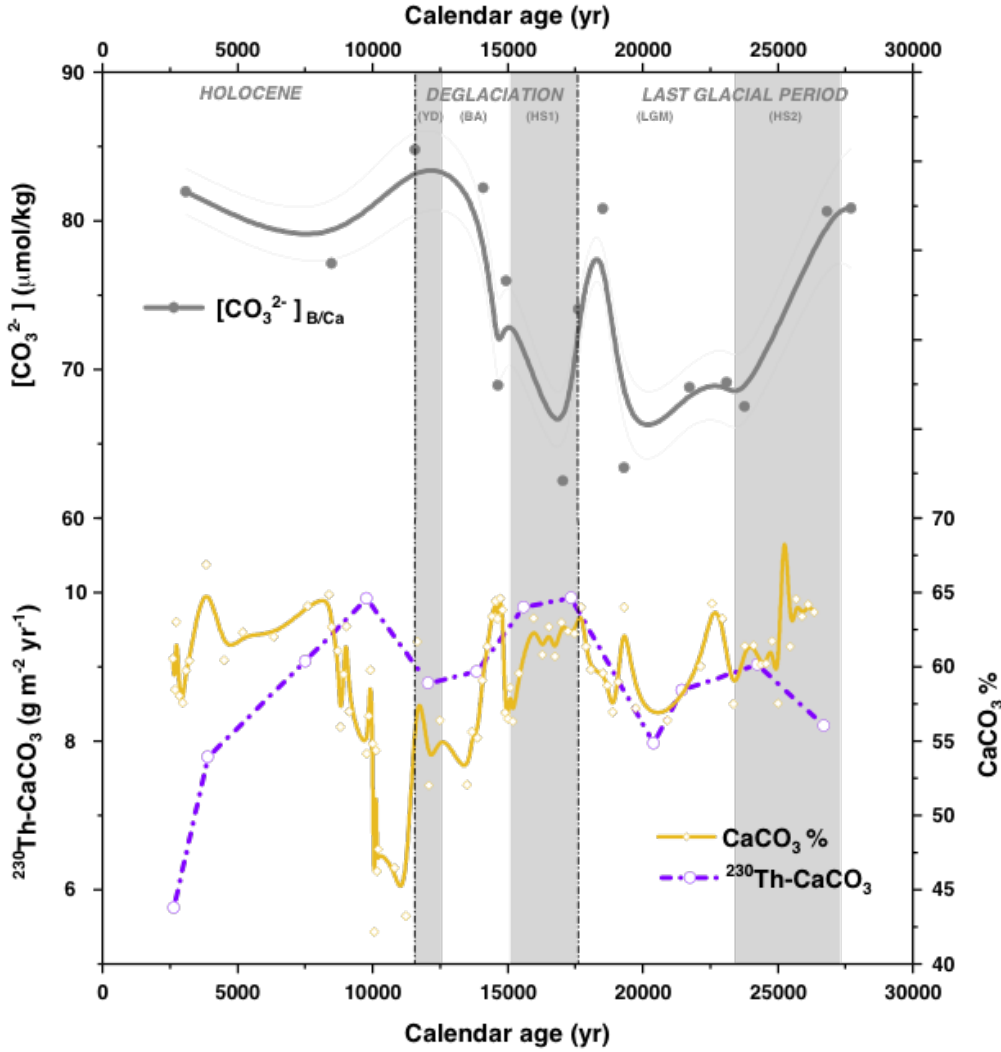


Figure 5. Carbonate chemistry-related records from core ODP1240 across the past 30 kyr. Upper panel: $[\text{CO}_3^{2-}]_{\text{B/Ca}}$ -based (grey line/dots; this study). Lower panel: $^{230}\text{Th-CaCO}_3$ and $\text{CaCO}_3\%$ (purple dashed line/open dots and yellow line/open diamonds, respectively; *Pichevin et al.*, [2009]). Vertical dashed lines delimit relevant climatic periods, and light grey vertical bands highlight the coldest periods of the last 30 kyr.

Despite no obvious carbonate dissolution in core ODP1240 being observed during the LGM, it remains possible that $[\text{CO}_3^{2-}]$ was added to deep waters bathing the EEP through carbonate dissolution elsewhere in the Pacific [*Anderson et al.*, 2008]. Indeed, similarly small $[\text{CO}_3^{2-}]$ differences between LGM-Holocene/modern have also been reported in other areas from the Pacific Ocean [*Yu et al.*, 2010; *Doss and Marchitto*, 2013; *Allen et al.*, 2015; *Elmore et al.*, 2015], and this has been generally attributed to the large buffering capacity of carbonate sediments in this basin [*Yu et al.*, 2010, 2013; *Allen et al.*, 2015]. In Figure 6, a compilation of the averaged $\Delta[\text{CO}_3^{2-}]$ offsets between the LGM ($\sim 18\text{--}23$ kyr) and the late Holocene ($\sim 0\text{--}8$ kyr) ($\Delta(\Delta[\text{CO}_3^{2-}])_{\text{LGM-Hol}}$) from these studies shows the consistency among the Indo-Pacific sites with variations of only ~ 5 $\mu\text{mol/kg}$ between these two periods (orange line in Figure 6). By restricting the comparison to LGM-Hol differences, potential biases due to different techniques/calibrations/standards can be avoided, as well as any biases that may arise from assuming constant local $[\text{CO}_3^{2-}]_{\text{sat}}$ across the deglaciation. Thus, negative values represent lower $\Delta[\text{CO}_3^{2-}]$ at the

LGM compared to the Holocene, while positive ones represent the opposite. The small LGM-late Holocene difference observed in the Indo-Pacific, in contrast with larger offsets detected within the Atlantic and Southern Oceans (blue line in Figure 6) [Yu *et al.*, 2008, 2013, 2014a, 2014b; Gottschalk *et al.*, 2015], still implies lower LGM $\Delta[\text{CO}_3^{2-}]$ for the whole Pacific as well as for the Atlantic and Southern Ocean at depths greater than $\sim 2,500$ m water depth. However, the $\Delta(\Delta[\text{CO}_3^{2-}])_{\text{LGM-Hol}}$ changes present a noticeable difference between basins above $\sim 2,500$ m water depth. This might point to the accumulation of respired DIC (i.e. not equilibrated with the atmosphere) in the Pacific, Southern Ocean and Atlantic $> 2,500$ m during the last glacial, and the maintenance of 'equilibrium' DIC [Ito and Follows, 2013] in Atlantic water masses shallower than $\sim 2,500$ m. The shallow Atlantic would thus have responded more closely to changes in the atmosphere, such that lower atmospheric CO_2 would be directly manifested as higher LGM $[\text{CO}_3^{2-}]$ [Hodell *et al.*, 2001; Yu *et al.*, 2008]. In this situation, seafloor CaCO_3 not only might have 'buffered' glacial $[\text{CO}_3^{2-}]$ changes in the EEP (without affecting $\delta^{13}\text{C}$ significantly), but also might have played a role in the atmospheric CO_2 drawdown during the LGM by contributing to increased average ocean alkalinity via $[\text{CO}_3^{2-}]$ supply to the ocean [Keir, 1995; Sigman and Boyle, 2000]. This would have further reinforced the effects of a higher biological pump efficiency achieved by circulation changes, and perhaps also by surface productivity changes.

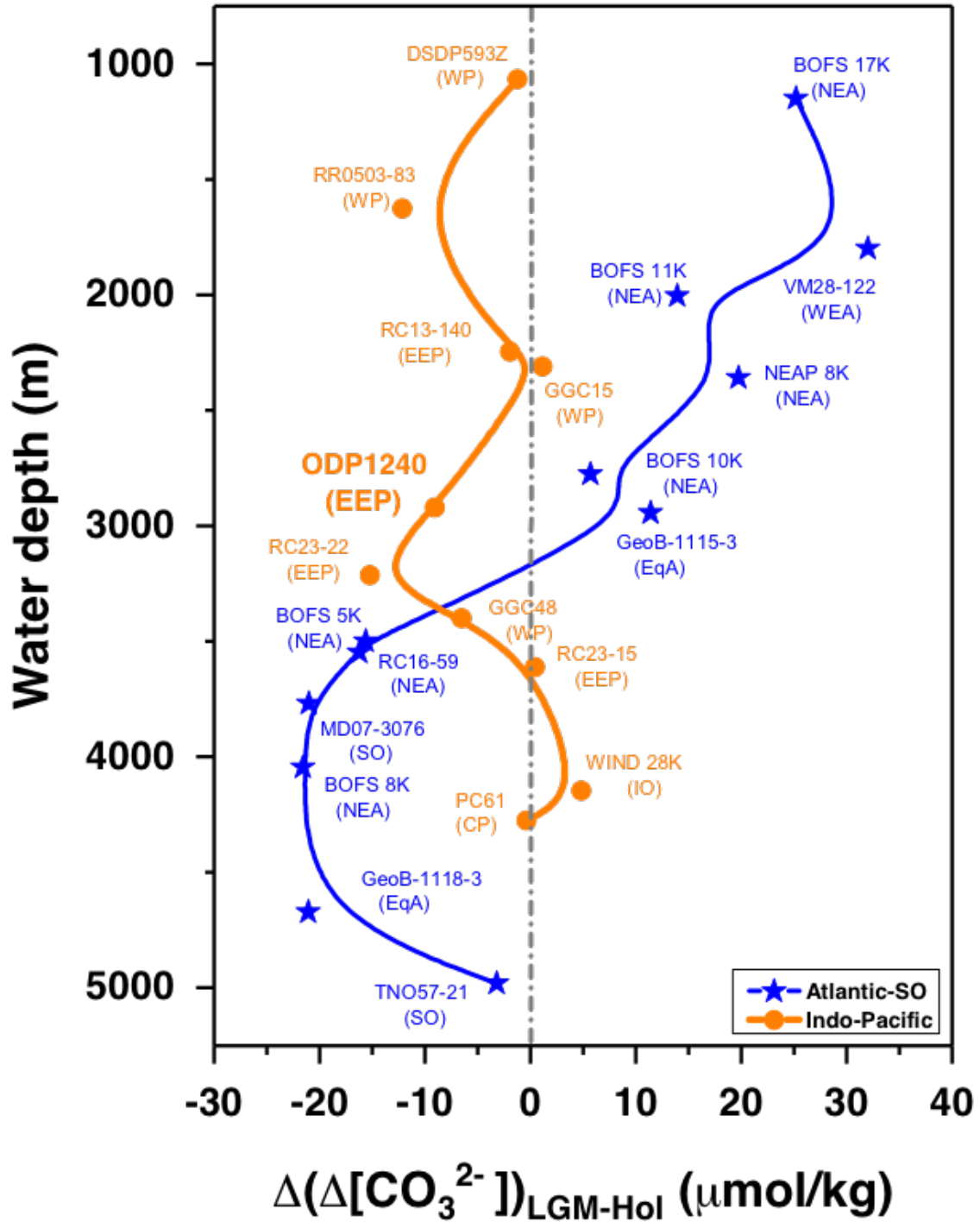


Figure 6. Deep water $[\text{CO}_3^{2-}]$ offset between LGM (~18-23 kyr) and Holocene/modern (~0-8 kyr) from several Atlantic/Southern Ocean (in blue) and Indo-Pacific Ocean (in orange) sediment cores. DSDP593Z [Elmore *et al.*, 2015], RR0503-83 [Allen *et al.*, 2015], MW91-9 GGC15, MW91-9 GGC48, WIND 28K and VM28-122 [Yu *et al.*, 2010], TTNO13 PC61, [Yu *et al.*, 2013], BOFS and NEAP cores [Yu and Elderfield, 2007; Yu *et al.*, 2008], RC13-140, RC23-22 and RC23-15 [Doss and Marchitto, 2013], RC16-59 [Broecker *et al.*, 2015], GeoB cores [Raitzsch *et al.*, 2011], MD07-3076 [Gottschalk *et al.*, 2015], TN057-21 [Yu *et al.*, 2014b] and ODP1240 (this study, highlighted in bold). WP: western Pacific; EEP: eastern equatorial Pacific; CP: central Pacific; NEA: North East Atlantic; WEA: western equatorial Pacific; EqA: equatorial Atlantic; SO: Southern Ocean; IO: Indian Ocean.

Interestingly, calculations based on the modern $\delta^{13}\text{C}$ - $[\text{CO}_3^{2-}]$ relationship in the Panama Basin suggest that the observed glacial-interglacial $\delta^{13}\text{C}$ difference is

compatible with the observed glacial-interglacial offset in $[\text{CO}_3^{2-}]$ (when a whole ocean glacial-interglacial $\delta^{13}\text{C}$ change of $\sim 0.3\text{‰}$ is assumed, due to terrestrial carbon release), which would imply no further $[\text{CO}_3^{2-}]$ addition from calcite dissolution [Doss and Marchitto, 2013]. Following the calculations of Doss and Marchitto, [2013], a $10\text{ }\mu\text{mol/kg}$ $[\text{CO}_3^{2-}]$ glacial-interglacial drop would achieve a $30\text{ }\mu\text{mol/kg}$ DIC increase, which in turn would produce a $\sim 0.26\text{‰}$ change in $\delta^{13}\text{C}$ due to respired carbon addition. If a whole ocean change of $\sim 0.3\text{‰}$ [Peterson *et al.*, 2014] is assumed to have occurred exclusively due to terrestrial carbon release [Shackleton, 1977], a total change of $\sim 0.56\text{‰}$ would therefore be expected, which is not very far off the results of Doss and Marchitto, [2013] and our observed glacial-interglacial $\delta^{13}\text{C}$ difference of $0.4 \pm 0.06\text{‰}$. However, it is notable that the observed global average glacial-interglacial $\delta^{13}\text{C}$ change of $\sim 0.3\text{‰}$ corresponds to a global average radiocarbon ventilation age change of perhaps $\sim 689\text{ }^{14}\text{C yr}$ [Skinner *et al.*, 2017], which raises the question of how this average change can be partitioned into a ‘terrestrial carbon component’ and a ‘ventilation/respired carbon component’. Until this issue is resolved, along with the related issue of how sub-aerial volcanism changed across the last glacial period [Broecker *et al.*, 2015], the possibility remains that much of the full glacial-interglacial $\delta^{13}\text{C}$ difference observed in ODP1240 was achieved by respired carbon addition, implying that a bigger drop in $[\text{CO}_3^{2-}]$ would be expected. This, in turn, would point to an additional process that would have counterbalanced the addition of $[\text{CO}_3^{2-}]$ from organic carbon respiration, such as CaCO_3 dissolution.

5. Conclusions

In this study, an increase in the biological pump efficiency over the LGM through a decrease in its leakiness has been investigated in the EEP as a mechanism for the glacial atmospheric CO_2 drawdown. The change in $[\text{CO}_3^{2-}]$, $\delta^{13}\text{C}$ and oxygenation proxies inferred in this study support this idea by presenting lower values in the EEP at the LGM compared to the late Holocene. However, the decrease in $[\text{CO}_3^{2-}]$ in this area is relatively small, suggesting that these mechanisms were not the only ones operating, or indeed contributing to the drop in glacial atmospheric CO_2 . This has also been observed in other Pacific $[\text{CO}_3^{2-}]$ records and has been suggested to be a consequence of larger carbonate dissolution over the LGM in this basin. Thus, respiratory calcite dissolution not only might explain the relatively small change in deep ocean $[\text{CO}_3^{2-}]$ between the glacial and late Holocene periods, but also would have likely and directly contributed to the glacial atmospheric CO_2 decrease by increasing the ocean average ALK and therefore decreasing the surface ocean $p\text{CO}_2$, thus allowing the surface ocean to take up more CO_2 . In conclusion, the deep EEP, and probably much of the wider deep Pacific, likely sequestered a significant amount of atmospheric CO_2 during the LGM, specifically due to a more efficient biological carbon pump caused by lower ventilation rates (and potentially also enhanced export production), but also due to an increase in average ocean alkalinity by respiratory calcite dissolution. However, a comparison with $\delta^{13}\text{C}$ data raises interesting questions regarding the relative contributions to the global marine carbon inventory during the last glacial period, from changes in deep ocean ventilation, export production, carbonate dissolution, terrestrial carbon release, and indeed volcanism. Further investigation in other basins using a

‘biogeochemical fingerprinting’ approach as applied in this study would help to address these questions, e.g. through better constraints on global average ocean chemistry changes at the LGM, which in turn would allow for a more accurate quantification of carbonate dissolution effects and marine CO₂ sequestration over this period.

6. References

- Allen, K. A., E. L. Sikes, B. Hönisch, A. C. Elmore, T. P. Guilderson, Y. Rosenthal, and R. F. Anderson (2015), Southwest Pacific deep water carbonate chemistry linked to high southern latitude climate and atmospheric CO₂ during the Last Glacial Termination, *Quat. Sci. Rev.*, *122*, 180–191, doi:10.1016/j.quascirev.2015.05.007.
- Anderson, L. a, and J. L. Sarmiento (1994), Redfield ratios of remineralization determined by nutrient data analysis, *Global Biogeochem. Cycles*, *8*(1), 65–80.
- Anderson, R. F., M. Q. Fleisher, Y. Lao, and G. Winckler (2008), Modern CaCO₃ preservation in equatorial Pacific sediments in the context of late-Pleistocene glacial cycles, *Mar. Chem.*, *111*(1–2), 30–46, doi:10.1016/j.marchem.2007.11.011.
- Archer, D. (1991), Equatorial Pacific calcite preservation cycles: production or dissolution?, *Paleoceanography*, *6*(5), 561–571.
- Archer, D. (1996), A data-driven model of the global calcite lysocline, *Global Biogeochem. Cycles*, *10*(3), 511–526.
- Archer, D., and E. Maier-Reimer (1994), Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration, *Nature*, *367*(6460), 260–263.
- Berelson, W. M. et al. (1997), Biogenic budgets of particle rain, benthic remineralization and sediment accumulation in the equatorial Pacific, *Deep Sea Res. Part II Top. Stud. Oceanogr.*, *44*(9–10), 2251–2282.
- Boiteau, R., M. Greaves, and H. Elderfield (2012), Authigenic uranium in foraminiferal coatings: A proxy for ocean redox chemistry, *Paleoceanography*, *27*(3), 1–8, doi:10.1029/2012PA002335.
- Bolton, A., J. a. Baker, G. B. Dunbar, L. Carter, E. G. C. Smith, and H. L. Neil (2011), Environmental versus biological controls on Mg/Ca variability in Globigerinoides ruber (white) from core top and plankton tow samples in the southwest Pacific Ocean, *Paleoceanography*, *26*(2), 1–14, doi:10.1029/2010PA001924.
- Boyle, E. A. (1983), Manganese carbonate overgrowths on foraminifera tests, *Geochim. Cosmochim. Acta*, *47*, 1815–1819.
- Bradtmitter, L., R. F. Anderson, M. Q. Fleisher, and C. Burk (2006), Diatom productivity in the equatorial Pacific Ocean from the last glacial period to the present: A test of the silicic acid leakage hypothesis, *Paleoceanography*, *21*(4), 1–12, doi:10.1029/2006PA001282.
- Bradtmitter, L., R. F. Anderson, J. P. Sachs, and M. Q. Fleisher (2010), A deeper respired carbon pool in the glacial equatorial Pacific Ocean, *Earth Planet. Sci. Lett.*, *299*(3–4), 417–425, doi:10.1016/j.epsl.2010.09.022.
- Broecker, W. S., and T -H. Peng (1987), The role of CaCO₃ compensation in the glacial

- to interglacial atmospheric CO₂ change, *Global Biogeochem. Cycles*, 1(1), 15–29, doi:10.1029/GB001i001p00015.
- Broecker, W. S., and T-H. Peng (1989), The cause of the glacial to interglacial atmospheric CO₂ change: A polar alkalinity hypothesis, *Global Biogeochem. Cycles*, 3(89), 215–239.
- Broecker, W. S., J. Yu, and A. E. Putnam (2015), Two contributors to the glacial CO₂ decline, *Earth Planet. Sci. Lett.*, 429, 191–196, doi:http://dx.doi.org/10.1016/j.epsl.2015.07.019.
- Brown, R. E., L. D. Anderson, E. Thomas, and J. Zachos (2011), A core-top calibration of B/Ca in the benthic foraminifers *Nuttallides umbonifera* and *Oridorsalis umbonatus*: A proxy for Cenozoic bottom water carbonate saturation, *Earth Planet. Sci. Lett.*, 310(3–4), 360–368, doi:10.1016/j.epsl.2011.08.023.
- Burke, A., and L. Robinson (2012), The Southern Ocean's role in carbon exchange during the last deglaciation, *Science*, 335(6068), 557–561.
- Calvo, E., C. Pelejero, L. D. Pena, I. Cacho, and G. a Logan (2011), Eastern equatorial pacific productivity and related-CO₂ changes since the last glacial period., *Proc. Natl. Acad. Sci. U. S. A.*, 108(14), 5537–41, doi:10.1073/pnas.1009761108.
- Cochran, J. K., A. E. Carey, E. Sholkovitz, and L. Surprenant (1986), The geochemistry of uranium and thorium in coastal marine sediments and sediment pore waters, *Geochim. Cosmochim. Acta*, 50(Vi), 663–680.
- Costa, K. M., J. F. McManus, R. F. Anderson, H. Ren, D. M. Sigman, G. Winckler, M. Q. Fleisher, F. Marcantonio, and A. C. Ravelo (2016), No iron fertilization in the equatorial Pacific Ocean during the last ice age, *Nature*, 529(7587), 519–522, doi:10.1038/nature16453.
- Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep Sea Res. Part A. Oceanogr. Res. Pap.*, 34(10), 1733–1743.
- Doss, W., and T. M. Marchitto (2013), Glacial deep ocean sequestration of CO₂ driven by the eastern equatorial Pacific biologic pump, *Earth Planet. Sci. Lett.*, 377–378, 43–54, doi:10.1016/j.epsl.2013.07.019.
- Eggins, S., L. P. J. Kinsley, and J. M. G. Shelley (1998), Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS, *Appl. Surf. Sci.*, 127–129, 278–286, doi:10.1016/S0169-4332(97)00643-0.
- Elmore, A. C., E. L. McClymont, H. Elderfield, S. Kender, M. R. Cook, M. J. Leng, M. Greaves, and S. Misra (2015), Antarctic Intermediate Water properties since 400 ka recorded in infaunal (*Uvigerina peregrina*) and epifaunal (*Planulina wuellerstorfi*) benthic foraminifera, *Earth Planet. Sci. Lett.*, 193–203, doi:10.1016/j.epsl.2015.07.013.
- Evans, D., and W. Müller (2013), LA-ICPMS elemental imaging of complex discontinuous carbonates: An example using large benthic foraminifera, *J. Anal. At. Spectrom.*, 28(7), 1039, doi:10.1039/c3ja50053e.
- Evans, D., B. Rehemat, H. Stoll, and W. Müller (2015), LA-ICPMS Ba/Ca analyses of planktic foraminifera from the Bay of Bengal: Implications for late Pleistocene orbital control on monsoon freshwater flux, *Geochemistry, Geophys. Geosystems*,

- 16, 2598–2618, doi:10.1002/2015GC005822.
- Flückiger, J., E. Monnin, B. Stauffer, J. Schwander, and T. F. Stocker (2002), High-resolution Holocene N₂O ice core record and its relationship with CH₄ and CO₂, *Global Biogeochem. Cycles*, 16(1).
- Gottschalk, J., L. Skinner, S. Misra, C. Waelbroeck, L. Menviel, and A. Timmermann (2015), Abrupt changes in the southern extent of North Atlantic Deep Water during Dansgaard–Oeschger events, *Nat. Geosci.*, 8, 950–955, doi:10.1038/ngeo2558.
- Gottschalk, J., L. Skinner, J. Lippold, H. Vogel, N. Frank, S. Jaccard, and C. Waelbroeck (2016), Biological and physical controls in the Southern Ocean on past millennial-scale atmospheric CO₂ changes, *Nat Commun*, 7.
- Hodell, D. a, C. D. Charles, and F. Sierro (2001), Late Pleistocene evolution of the ocean’s carbonate system, *Earth Planet. Sci. Lett.*, 192(2), 109–124, doi:10.1016/S0012-821X(01)00430-7.
- Hoogakker, B. a. a., H. Elderfield, G. Schmiedl, N. I. McCave, and R. E. M. Rickaby (2014), Glacial–interglacial changes in bottom-water oxygen content on the Portuguese margin, *Nat. Geosci.*, 8(1), 40–43, doi:10.1038/ngeo2317.
- Ito, T., and M. J. Follows (2013), Air-sea disequilibrium of carbon dioxide enhances the biological carbon sequestration in the Southern Ocean, *Global Biogeochem. Cycles*, 27(4), 1129–1138, doi:10.1002/2013GB004682.
- Jaccard, S., E. Galbraith, A. Martínez-García, and R. F. Anderson (2016), Covariation of deep Southern Ocean oxygenation and atmospheric CO₂ through the last ice age, *Nature*, 530(7589), 207–210, doi:10.1038/nature16514.
- Jochum, K. P. et al. (2006), MPI-DING reference glasses for in situ microanalysis: New reference values for element concentrations and isotope ratios, *Geochemistry Geophys. Geosystems*, 7(2), doi:10.1029/2005GC001060.
- Jochum, K. P. et al. (2011), Determination of Reference Values for NIST SRM 610-617 Glasses Following ISO Guidelines, *Geostand. Geoanalytical Res.*, 35(4), 397–429, doi:10.1111/j.1751-908X.2011.00120.x.
- Keir, R. S. (1995), Is there a component of Pleistocene CO₂ change associated with carbonate dissolution cycles?, *Paleoceanography*, 10(5).
- Kessler, W. (2006), The circulation of the eastern tropical Pacific: A review, *Prog. Oceanogr.*, 69(2–4), 181–217, doi:10.1016/j.pocean.2006.03.009.
- Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. a Feely, F. J. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, 18(4), 1–23, doi:10.1029/2004GB002247.
- Kienast, M., S. Kienast, S. E. Calvert, T. I. Eglinton, G. Mollenhauer, R. François, and A. Mix (2006), Eastern Pacific cooling and Atlantic overturning circulation during the last deglaciation, *Nature*, 443(7113), 846–9, doi:10.1038/nature05222.
- Kienast, S., M. Kienast, A. Mix, S. E. Calvert, and R. François (2007), Thorium-230 normalized particle flux and sediment focusing in the Panama Basin region during the last 30,000 years, *Paleoceanography*, 22(2), 1–19, doi:10.1029/2006PA001357.
- Kohfeld, K. E., and A. Ridgwell (2009), Glacial-interglacial variability in atmospheric

- CO₂, *Surf. Ocean Low. Atmos. Process.*, 187, 251–286.
- Kwon, E. Y., F. Primeau, and J. L. Sarmiento (2009), The impact of remineralization depth on the air–sea carbon balance, *Nat. Geosci.*, 2(9), 630–635, doi:10.1038/ngeo612.
- de la Fuente, M., L. Skinner, E. Calvo, C. Pelejero, and I. Cacho (2015), Increased reservoir ages and poorly ventilated deep waters inferred in the glacial Eastern Equatorial Pacific, *Nat. Commun.*, 6, doi:10.1038/ncomms8420.
- Langmuir, D. (1978), Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, *Geochim. Cosmochim. Acta*, 42(6), 547–569, doi:10.1016/0016-7037(78)90001-7.
- Lemieux-Dudon, B., E. Blayo, J.-R. Petit, C. Waelbroeck, A. Svensson, C. Ritz, J. Barnola, B. M. Narcisi, and F. Parrenin (2010), Consistent dating for Antarctic and Greenland ice cores, *Quat. Sci. Rev.*, 29(1–2), 8–20, doi:10.1016/j.quascirev.2009.11.010.
- Lewis, E., D. Wallace, and L. J. Allison (1998), *Program developed for CO₂ system calculations*, Carbon Dioxide Information Analysis Center, managed by Lockheed Martin Energy Research Corporation for the US Department of Energy.
- Longerich, H. P., S. E. Jackson, and D. Günther (1996), Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation, *J. Anal. At. Spectrom.*, 11(9), 899–904, doi:10.1039/JA9961100899.
- Mantyla, A. W., and J. L. Reid (1983), Abyssal characteristics of the World Ocean waters, *Deep Sea Res. Part A, Oceanogr. Res. Pap.*, 30(8), 805–833, doi:10.1016/0198-0149(83)90002-X.
- Marr, J. P., J. a. Baker, L. Carter, A. S. R. Allan, G. B. Dunbar, and H. C. Bostock (2011), Ecological and temperature controls on Mg/Ca ratios of *Globigerina bulloides* from the southwest Pacific Ocean, *Paleoceanography*, 26(2), 1–15, doi:10.1029/2010PA002059.
- Martínez-García, A., D. M. Sigman, H. Ren, R. F. Anderson, M. Straub, D. a Hodel, S. Jaccard, T. I. Eglinton, and G. H. Haug (2014), Iron fertilization of the Subantarctic ocean during the last ice age, *Science*, 343, 1347–50, doi:10.1126/science.1246848.
- McCorkle, D. C., and S. R. Emerson (1988), The relationship between pore water carbon isotopic composition and bottom water oxygen concentration, *Geochim. Cosmochim. Acta*, 52(5), 1169–1178, doi:10.1016/0016-7037(88)90270-0.
- McGee, D., F. Marcantonio, and J. Lynch-Stieglitz (2007), Deglacial changes in dust flux in the eastern equatorial Pacific, *Earth Planet. Sci. Lett.*, 257(1–2), 215–230, doi:10.1016/j.epsl.2007.02.033.
- Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytowicz (1973), Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, 18, 897–907.
- Monnin, E., A. Indermühle, A. Dällenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J. Barnola (2001), Atmospheric CO₂ concentrations over the last glacial termination, *Science*, 291(5501), 112–4, doi:10.1126/science.291.5501.112.

- Morford, J. L., and S. Emerson (1999), The geochemistry of redox sensitive trace metals in sediments, *Geochim. Cosmochim. Acta*, 63(11–12), 1735–1750, doi:10.1016/S0016-7037(99)00126-X.
- Müller, W., J. M. G. Shelley, P. Miller, and S. Broude (2009), Initial performance metrics of a new custom-designed ArF excimer LA-ICPMS system coupled to a two-volume laser-ablation cell, *J. Anal. At. Spectrom.*, 24(2), 209, doi:10.1039/b805995k.
- Müller, W., and J. Fietzke (2016), The role of LA-ICP-MS in palaeoclimate research, *Elements*, 12(5), 329–334, doi:10.2113/gselements.12.5.329.
- Pedersen, T. F. (1983), Increased productivity in the eastern equatorial Pacific during the last glacial maximum (19,000 to 14,000 yr B.P.), *Geology*, 11, 16–19, doi:10.1130/0091-7613(1983)11<16.
- Peterson, C. D., L. Lisiecki, and J. V. Stern (2014), Deglacial whole-ocean $\delta^{13}\text{C}$ change estimated from 480 benthic foraminiferal records, *Paleoceanography*, 29, 549–563.
- Pichevin, L., B. C. Reynolds, R. S. Ganeshram, I. Cacho, L. D. Pena, K. Keefe, and R. M. Ellam (2009), Enhanced carbon pump inferred from relaxation of nutrient limitation in the glacial ocean, *Nature*, 459(7250), 1114–7, doi:10.1038/nature08101.
- Pierrot, D., E. Lewis, and D. W. R. Wallace (2006), MS Excel program developed for CO_2 system calculations, *ORNL/CDIAC-105a. Carbon Dioxide Inf. Anal. Center, Oak Ridge Natl. Lab. US Dep. Energy, Oak Ridge, Tennessee*.
- Rae, J. W. B., G. L. Foster, D. N. Schmidt, and T. Elliott (2011), Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system, *Earth Planet. Sci. Lett.*, 1–11, doi:10.1016/j.epsl.2010.12.034.
- Raitzsch, M., E. C. Hathorne, H. Kuhnert, J. Groeneveld, and T. Bickert (2011), Modern and late Pleistocene B/Ca ratios of the benthic foraminifer *Planulina wuellerstorfi* determined with laser ablation ICP-MS, *Geology*, 39(11), 1039–1042, doi:10.1130/G32009.1.
- Redfield, A. C., B. H. Ketchum, and F. A. Richards (1963), The influence of organisms on the composition of sea-water, *The sea*, 2, 26–77.
- Reimer, P. J., M. G. L. Baillie, E. Bard, A. Bayliss, J. Berk, P. G. Blackwell, C. Bronk Ramsey, C. Burk, and G. S. Burr (2009), IntCal09 and marine09 radiocarbon age calibration curves, 0–50,000 years cal BP, *Radiocarbon*, 51(4), 1111–1150.
- Robinson, R., P. Martinez, L. D. Pena, and I. Cacho (2009), Nitrogen isotopic evidence for deglacial changes in nutrient supply in the eastern equatorial Pacific, *Paleoceanography*, 24(4), 1–12, doi:10.1029/2008PA001702.
- Sarmiento, J. L., and N. Gruber (2004), *Ocean Biogeochemical Dynamics*.
- Schlitzer, R. (2017), Ocean Data View, <http://odv.awi.de>.
- Shackleton, N. J. (1977), Carbon-13 in *Uvigerina*: Tropical rain forest history and the equatorial Pacific carbonate dissolution cycle, in *The Fate of Fossil Fuel in the Oceans*, edited by N. R. Andersen and A. Malahoff, pp. 401–427, Plenum, New York.
- Siani, G., E. Michel, R. De Pol-Holz, T. Devries, F. Lamy, M. Carel, G. Isguder, F. Dewilde, and A. Lourantou (2013), Carbon isotope records reveal precise timing of

- enhanced Southern Ocean upwelling during the last deglaciation, *Nat. Commun.*, *4*, doi:10.1038/ncomms3758.
- Sigman, D. M., and E. A. Boyle (2000), Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, *407*, 859–869.
- Sigman, D. M., M. P. Hain, and G. H. Haug (2010), The polar ocean and glacial cycles in atmospheric CO₂ concentration, *Nat. Rev.*, *466*(7302), 47–55, doi:10.1038/nature09149.
- Sikes, E. L., C. R. Samson, T. P. Guilderson, and W. R. Howard (2000), Old radiocarbon ages in the southwest Pacific Ocean during the last glacial period and deglaciation, *Nature*, *303*, 555–559.
- Skinner, L., S. J. Fallon, C. Waelbroeck, E. Michel, and S. Barker (2010), Ventilation of the deep Southern Ocean and deglacial CO₂ rise, *Science*, *328*(5982), 1147–51, doi:10.1126/science.1183627.
- Skinner, L., N. I. McCave, L. Carter, S. J. Fallon, A. Scrivner, and F. Primeau (2015), Reduced ventilation and enhanced magnitude of the deep Pacific carbon pool during the last glacial period, *Earth Planet. Sci. Lett.*, *411*, 45–52, doi:10.1016/j.epsl.2014.11.024.
- Skinner, L. C. L. et al. (2017), Radiocarbon constraints on the glacial ocean circulation and its impact on atmospheric CO₂, *Nat. Commun.*, *8*(May), 1–10, doi:10.1038/ncomms16010
- Stephens, B. B., and R. F. Keeling (2000), The influence of Antarctic sea ice on glacial-interglacial CO₂ variations, *Nature*, *404*, 171–174.
- Strub, P., J. Mesías, V. Montecino, J. Rutlant, and S. Salinas (1998), Coastal ocean circulation off western South America, Costal segment (6,E), in *The sea, Vol 11*, edited by A. R. Robinson and K. H. Brink, pp. 273–314, John Wiley & Sons, Inc, New York.
- Talley, L. D., G. L. Pickard, W. J. Emery, and J. H. Swift (2011), *Descriptive Physical Oceanography: An introduction*, 6th ed., Elsevier, Boston.
- Toggweiler, J. R. (1999), Variation of atmospheric CO₂ by ventilation of the ocean's deepest water, *Paleoceanography*, *14*(5), 571–588.
- Tsuchiya, M., and L. D. Talley (1998), A Pacific hydrography section at 88°W: Water-property distribution, *J. Geophys. Res.*, *103*(C6), 12,899–12,918.
- Umling, N. E., and R. C. Thunell (2017), Synchronous deglacial thermocline and deep-water ventilation in the eastern equatorial Pacific, *Nat. Commun.*, *8*, doi:10.1038/ncomms14203.
- Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂ changes, *Geophys. Monogr. Ser.*, *32*, 99–110.
- Williams, R. G., and M. J. Follows (2011), *Ocean dynamics and the carbon cycle: Principles and mechanisms*, Cambridge University Press.
- Winckler, G., R. F. Anderson, S. Jaccard, and F. Marcantonio (2016), Ocean dynamics, not dust, have controlled equatorial Pacific productivity over the past 500,000 years, *Proc. Natl. Acad. Sci.*, 201600616, doi:10.1073/pnas.1600616113.

- You, Y. (2000), Implications of the deep circulation and ventilation of the Indian Ocean on the renewal mechanism of North Atlantic Deep Water, *J. Geophys. Res.*, *105*, 23,895–23,926.
- Yu, J., and H. Elderfield (2007), Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, *Earth Planet. Sci. Lett.*, *258*(1–2), 73–86, doi:10.1016/j.epsl.2007.03.025.
- Yu, J., H. Elderfield, and A. M. Piotrowski (2008), Seawater carbonate ion- $\delta^{13}\text{C}$ systematics and application to glacial–interglacial North Atlantic ocean circulation, *Earth Planet. Sci. Lett.*, *271*(1–4), 209–220, doi:10.1016/j.epsl.2008.04.010.
- Yu, J., W. S. Broecker, H. Elderfield, Z. Jin, J. F. McManus, and F. Zhang (2010), Loss of carbon from the deep sea since the Last Glacial Maximum, *Science*, *330*(6007), 1084–1087, doi:10.1126/science.1193221.
- Yu, J., R. F. Anderson, Z. Jin, J. W. B. Rae, B. N. Opdyke, and S. Eggins (2013), Responses of the deep ocean carbonate system to carbon reorganization during the Last Glacial–interglacial cycle, *Quat. Sci. Rev.*, *76*, 39–52, doi:10.1016/j.quascirev.2013.06.020.
- Yu, J., R. F. Anderson, and E. J. Rohling (2014a), Deep ocean carbonate chemistry and glacial–interglacial atmospheric CO_2 changes, *Oceanography*, *27*(1), 16–25.
- Yu, J., R. F. Anderson, Z. Jin, L. Menviel, F. Zhang, F. J. Ryerson, and E. J. Rohling (2014b), Deep South Atlantic carbonate chemistry and increased interocean deep water exchange during last deglaciation, *Quat. Sci. Rev.*, *90*, 80–89, doi:10.1016/j.quascirev.2014.02.018.
- Yu, J. et al. (2016), Sequestration of carbon in the deep Atlantic during the last glaciation, *Nat. Geosci.*, *9*(4), 319–324, doi:10.1038/ngeo2657.
- Zeebe, R., and D. A. Wolf-Gladrow (2001), *CO_2 in seawater: equilibrium, kinetics, isotopes*, 65, Gulf Professional Publishing.

7. Acknowledgements

We would like to thank Aleksey Sadekov for insightful discussions on B/Ca analysis by LA-ICPMS. The crew of the R/V James Cook are thanked for their support during cruise JC089, and David Hodell for access to core-top samples and pore-water data from the Iberian Margin. For the rest of the core-top samples, their supply and advise on them, we thank Fiz F. Pérez, Guillermo Francés, Leopoldo Pena and Anna Sánchez. We are also grateful for the assistance of Viola Warter with LA-ICPMS, Adam Scrivner and Salima Souanef-Ureta with U/Ca analyses, James Rolfe with $\delta^{13}\text{C}$ measurements and Jesus Peña-Izquierdo for help with the hydrography of the study area. This work also benefited from discussions made possible by the INQUA ‘IPODS’ (Investigating Past Ocean Dynamics) focus group. We acknowledge funding by the Spanish Ministry of Economy and Competitiveness through grants CTM2009-08849 (ACDC Project) and CTM2012-32017 (MANIFEST Project), by Generalitat de Catalunya through Grant 2014SGR1029 (Marine Biogeochemistry and Global Change research group), and by NERC grant NE/L006421/1. Isabel Cacho thanks the ICREA Academia program from the Generalitat de Catalunya. All data are included as spreadsheets in the supporting information.